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Research Article

Green Synthesis of Gold Nanoparticles using *Pimenta dioica* Leaves Aqueous Extract and Their Application as Photocatalyst, Antioxidant, and Antibacterial Agents

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Abstract

Green synthesis of gold nanoparticles (AuNPs) is of particular interest due to their catalytic, antioxidant, and antibacterial properties. In this study, the aqueous extract of *Pimenta dioica* leaves was used to synthesize AuNPs and the effective parameters were investigated. The prepared AuNPs were characterized by various techniques including UV–Vis absorption spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), and X-ray diffractometer (XRD). The reduction and stabilization effect of the plant extract to fabricate AuNPs were explained by FTIR analysis. TEM imaging confirmed the formation of spherical-shaped AuNPs. The catalytic activity of synthesized nanoparticles was evaluated in the degradation of a Methylene Blue dye in the presence of $NaBH_4$ as reducing agent and achieved after only two minutes. The AuNPs provided high antioxidant ability. In addition, the synthesized AuNPs showed a significant inhibitory effect against both gram-positive and gram-negative bacteria, where the zone of inhibition of 4 and 9 mm were obtained for synthesized AuNPs against *S. aureus* and *E. coli*, respectively.

Keywords: antibacterial, antioxidant, catalyst, gold nanoparticles, *Pimenta dioica*

1. INTRODUCTION

Researchers are interested in gold nanoparticles (AuNPs) because of their applications in optoelectronic [1], electrical [2], and magnetic devices [3], as well as catalysis [4]–[6], sensors [7]–[9], and drug delivery [10]. Form, size, crystallinity, and structure are all important factors in these applications. Gold nanostructures have been identified in a variety of shapes, including nanocubes [11], nanowires [12], nanoplates [13], nanospheres, nanorods [14], nanopores [15], nanobelts, and odd angled shapes [16]. Many groups of researchers have long been interested in one-dimensional (1D) metallic nanostructures. The researchers were drawn to AuNPs because of their unusual and tunable surface plasmon resonance. Because of their non-cytotoxicity and biocompatibility, AuNPs have become more common in biomedical applications than other metallic nanostructures [17]. AuNPs are simple to make and have excellent chemical and thermal stability. Because of their unusual biocompatibility and well-defined surface chemistry, AuNPs have been used as detection methods in molecular imaging using fluorescence resonance energy transfer [18].

Due to its unique characteristics such as safety, environmental friendliness, and cost-effectiveness, green synthesis of gold nanoparticles (AuNPs) has gotten a lot of attention [19][20]. For the synthesis of AuNPs, various physical and chemical methods have already been used [21]–[23]. Most of the approaches are time-consuming, involve a multi-step synthesis procedure, and involve the use of harmful organic and inorganic chemicals [22]. The existence of these toxic chemicals in trace amounts on the surfaces of fabricated AuNPs is a possibility, which would restrict their biomedical applications. As a result, a method to synthesize biocompatible AuNPs that is both environmentally friendly and free of toxic chemicals is needed. Plant-mediated green synthesis is an environmentally friendly method for producing monodisperse and chemically stable AuNPs of various sizes and shapes. Plant phytochemicals or biomolecules play a key role in the reduction of metal ions during this synthesis phase [24].

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Pimenta dioica (L.), also known as allspice, belongs to the Myrtaceae family. *P. dioica* has anesthetic, antiseptic, antihelmintic, febrifuge, and antiseptic properties. *P. dioica* dried fruits are a valuable spice used all over the world. The therapeutic properties of *P. dioica* fragrance oils include antioxidant, antimicrobial, tonic, hypotensive activity, anti-inflammatory, and anthelmintic properties [25].

Pimenta *dioica* has been used in the preparation of silver nanoparticles in previous studies [26]. Carbohydrate, protein, steroid, alkaloid, flavonoids, phenol, and terpenoids were detected in the ethanolic extract; protein, phenol, and terpenoids were detected in the diethyl ether extract; and carbohydrate, alkaloid, flavonoids, steroids, saponins, tannin, and terpenoids were detected in the aqueous extract. By using a ferrous ion chelating assay, a nitric oxide radical scavenging assay, and a DPPH test, the antioxidant content of *P. dioica* leaf extract was determined. The occurrence of carboxylic acid, alkyl halides alkanes, and miscellaneous functional groups in *P. dioica* leaves have been reported by Murali et al. [27]. Kharey et al. [28] obtain green synthesized gold nanoparticles (AuNPs) using aqueous leaf extract of *Pimenta dioica*. Using MTT (3-(4,5-dimethylthiozol-2-yl)-2,5-diphenyl tetrazolium bromide) assay, synthesized AuNPs safe for human cervical cancer (HeLa) and human embryonic kidney 293 (HEK 293) cell lines. Further, the synthesized AuNPs showed excellent photoacoustic signal responses (PASR) and found to be the most efficient photoacoustic signal generators.

As a result, the aim of this study was to synthesize AuNPs from *Pimenta dioica* leaf aqueous extract without using any other chemicals. Several spectral and microscopic methods revealed the formation of NPs. The effectiveness of AuNPs in reducing the organic dye pollutant methylene blue (MB) was also investigated. At the same time, antioxidant and antibacterial properties of the synthesized AuNPs were examined.

2. MATERIALS AND METHOD

2.1. Materials

Pimenta dioica leaves were freshly collected from Lapai, Nigeria. Gold (III) chloride tri-hydrate ($HAuCl_4.3H_2O$), 2,2-Diphenyl-1-picrylhydrazyl (DPPH), Methylene blue dyes (MB) and sodium borohydride ($NaBH_4$) were obtained from Sigma-Aldrich. Deionized ultra-pure water was used for preparing all respective solutions.

2.2. Methods

2.2.1. Preparation of aqueous extract

Under strict sterile conditions, about 25 g of fresh *Pimenta dioica* leaves were softened in a mortar and pestle and filtered through muslin cloth. In a clean and fresh glass bottle, the filtrate was collected. This filtrate will be kept cold for further examination. Around 5 g of leaves were crushed and mixed with 10 ml of Deionized ultra-pure water before being ground. The extraction process took three hours and was held overnight. The solution was filtered the next day, and the filtrate was processed for further analysis.

2.2.2. Biosynthesis of AuNPs by P. dioica leaves aqueous extract

The reduction of Au^{3+} to Au^0, as described by Jayaseelan et al. [29], was used to produce AuNPs mediated by *Pimenta dioica* extract. 40 ml of *Pimenta dioica* leaves aqueous extract was added to 60 ml of 1 mM aqueous $HAuCl_4.3H_2O$ solution and the solution was placed in orbital shaker at room temperature, for reduction of Au^{3+} to Au^0. The bio-reduction of the gold ions in the solution was monitored periodically by measuring the UV–visible spectroscopy of the solutions. The reaction was rapid as the ruby red color appeared within 10 min and the reaction confirmed the formation of Au NPs and there was no color change further. The

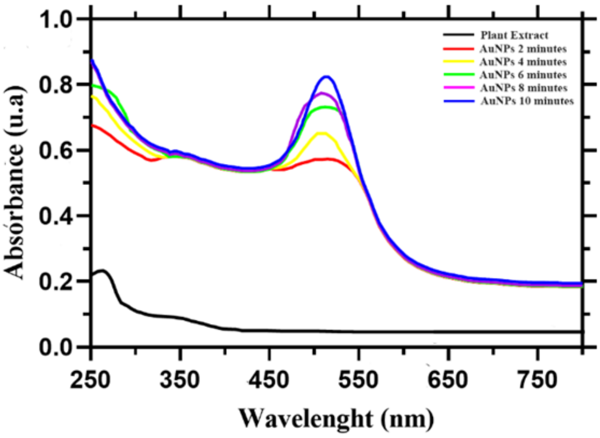

Figure 1. UV–visible spectrum of synthesized AuNPs showed peak at 536 nm

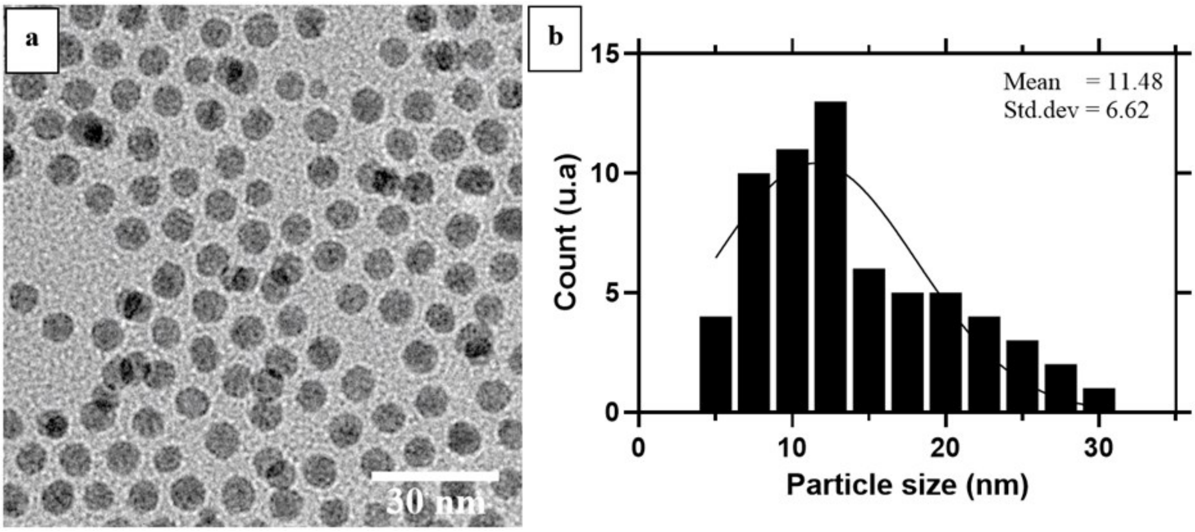

Figure 2. (a) TEM image and (b) particle size distribution of synthesized AuNPs

control leaves aqueous extract of *Pimenta dioica* did not show any change in color. The optimum time required for the completion of reaction was 10 min. Different concentration of $HAuCl_4$ solution was used to get maximum AuNPs. The overall optimized reaction condition was observed in 1 mM $HAuCl_4$ solution and neutral pH. The AuNPs obtained from the solution were purified by repeated centrifugation at 2000 rpm for 10 min followed by dispersion of the pellet thrice in deionized ultra-pure water to remove the water-soluble biomolecules such as proteins and secondary metabolites. The water suspended AuNPs were frozen at 30 °C overnight and then kept under vacuum for 24 h to dry the AuNPs.

2.2.3. Characterization

The morphology of the synthesized NPs (including nanoscale, shape, and uniformity) was investigated by TEM microscope, (JEOL, model JEM-2010) with an accelerating voltage of 200 kV. The optical absorbance of the as-prepared NPs solutions was measured by UV–Vis Spectrophotometer (Shimadzu UV-2450 spectrophotometer, one cm wide quartz cells). The structural information and types of functional groups from the extract that may be involved in the synthesis and stabilization of AuNPs were obtained by FTIR spectrophotometer (JASCO spectrometer) over the 4000 to 400 cm^{-1} range. The particle size range of the nanoparticles were determined by using particle size analyzer (Malvern Zetasizer nanosizer).

2.2.4. The photocatalytic activity

The photocatalytic activity of AuNPs was assessed by investigating the reduction of MB dye via $NaBH_4$, whereas the biologically as-synthesized AuNPs were utilized as a catalyst at 25 ºC under solar light. The procedure started by adding 2.5 mL of 0.08 mM MB dye solutions in a one cm path length quartz cuvette. Then, 0.5 mL of freshly prepared $NaBH_4$ (0.06 M) solution was added to the dye solution, followed by the addition of 0.5 mL of colloidal AuNPs. Afterward, the solution was subjected to solar light under gentle stirring. The dye’s reduction reaction was monitored by recording changes in the MB absorption after one minute using the following Equation 1 [24]:

$$\text{degradation rate } (\%) = \frac{(Co - C)}{Co} x100\% \tag{1}$$

While, Co = initial concentration of dye, C = the concentration of dye upon irradiation.

2.2.5. The Antioxidant efficiency

The free radical scavenging potential of the plant extract and prepared NPs were assessed using DPPH, according to Amrulloh et al. [30] method. Briefly, the synthesized AuNPs solution (different volume 10, 20, 30, 40, and 50 µl) was mixed with 1000 µl of DPPH (0.2 mM). A DPPH solution without NPs was also examined and utilized as a negative control. Additionally, the test was also made on two-fold-diluted solutions of each sample. After that, the DPPH solutions were blended for 20 min at ambient temperature in a dark condition. At

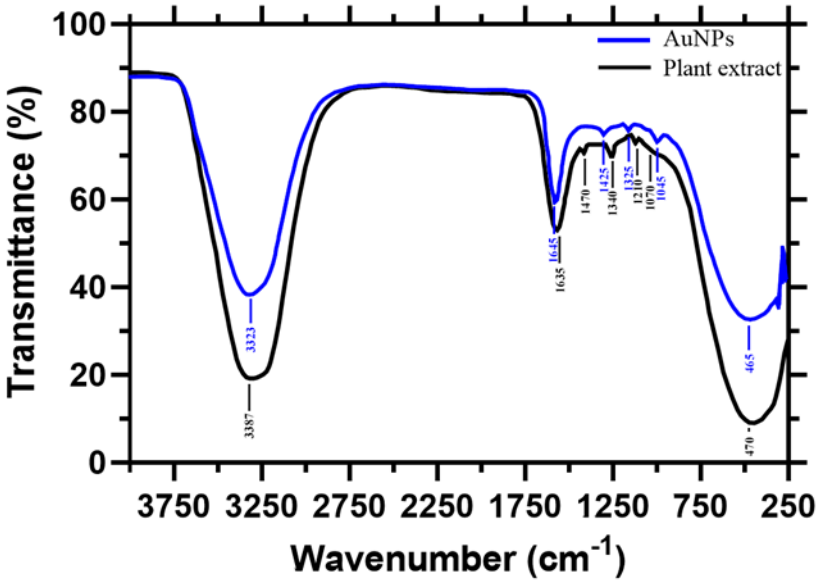

Figure 3. FTIR spectrum of synthesized AuNPs and *P. dioica* leaves aqueous extract

the end of the incubation period, the radical concentration was determined by following the reduction in its absorbance percentage at a specific wavelength of 517 nm. The scavenging efficiency was expressed as the inhibition percent of DPPH radicals, and it was calculated according to the following Equation 2 [24]:

$$\% \; inhibition = \frac{control\ absorbance\ \text{-}\ sample\ absorbance}{control\ absorbance} \; x \; 100\% \qquad (2)$$

2.2.6. The antibacterial assays

Antibacterial activity was analyzed with synthesized gold nanoparticles by well diffusion method against clinically isolated Gram negative (*Escherichia coli*) and Gram positive (*Staphylococcus aureus*) microorganisms. The pathogenic cultures were bringing into broth culture for antibacterial assay. Approximately 7-mm diameter of well was made on Muller Hinton Agar plate with the help of gel puncture. The cultures were swabbed on test media with sterile cotton swab. Various volume (10, 20, 30, 40, and 50 µl) of synthesized AuNPs were inoculated to the well, and then the plates were incubated in incubator for 37 ° C for 24 h, the zones of inhibition indicated the antibacterial activity was measured in mm.

3. RESULT AND DISCUSSION

3.1. Spectral, morphological, and structural characterization

3.1.1. UV-Visible spectroscopy, TEM, and PSA

The green synthesis of AuNPs using environmental and nontoxic chemicals is the current approach. One of the most frequently used materials in green synthesis is the plant extract, which contains functional groups that can reduce Au^{3+} to Au^0. The UV–visible absorption spectra findings demonstrates a novel technique for the preparation of the Au NPs. The scale of wavelength was fixed between 250 and 800 nm, the surface plasmon resonance (SPR) of the AuNPs formed corresponded to 536 nm and there was an increase in intensity till 10 min as a function of time without any shift in the peak wavelength (Figure 1). It can be observed that the reduction of gold ions reaches saturation within 10 min of reaction, and after that, only slight variations can be noted in the intensity of SPR bands [24]. This result indicates that the reaction is completed in 10 min.

TEM images precisely reveal the morphological tuning with perpetual changes in synthesis conditions. Figure 2 shows TEM images of AuNPs. The particle size distributions of colloids AuNPs from PSA result are depicted in the histograms. The average particle size measured for AuNPs colloids is 11.48 nm.

3.1.2. FTIR spectroscopy and X-ray diffraction analysis

FTIR analysis was used to identify the possible bio-reducing biomolecules in the extract [31]. The

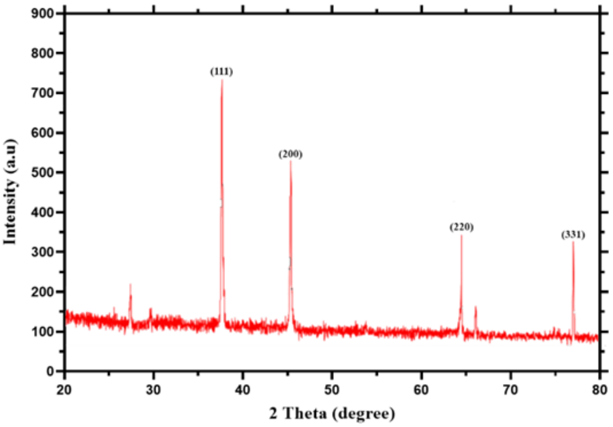

Figure 4. XRD pattern of synthesized AuNPs

presence of functional groups on the surface of AuNPs was identified by the FTIR measurement of synthesized AuNPs. FTIR spectra of AuNPs and plant extract are displayed in Figure 3. The major peaks were found at 3387, 1635, 1470, 1340, 1210, and 1070 cm^{-1} respectively. The peak at 3387 cm^{-1} indicates the presence of OH (phenolic/aliphatic hydroxyl) group. The peak at 1635 cm^{-1} represents the –C=C stretching of the alkene bond in eugenol. The peak at 1470 cm^{-1} corresponds to –C–C bond of an aromatic ring. The peaks at 1340, 1210, and 1070 cm^{-1} correspond to the asymmetric and symmetric C–O–C stretching mode, respectively, which confirms the presence of the methoxy group on the benzene ring of eugenol [32]–[34]. These peaks are consistent with the FTIR peaks of functional groups of eugenol, present in the *Pimenta dioica* plant [28].

The FTIR spectrum of AuNPs shows the peaks at 3323, 1645, 1425, 1325, and 1045 cm^{-1} respectively. A minor wavelength shift is observed in the peaks of the functional groups that were present in the extract before and after the nanoparticle formation. This peak shift could be attributed to the interaction of functional groups in *Pimenta dioica* plant extract with the nanoparticles. The strong band at 3323 cm^{-1} is the characteristic band of phenolic compound and the weak band at 1645 cm^{-1} corresponds to the alkene group of eugenol constituent of plant extract [35]. Results suggested that eugenol not only helps in the reduction of gold ions but also stabilizes the AuNPs [36].

The structural phase of the AuNPs formed were studied through XRD analysis. Figure 4 shows the strong and narrow diffraction peaks indicated that the product has well crystalline. The XRD peaks at 38, 44, 64 and 77 (º 2theta) can be indexed to the (111), (200), (220) and (311) Bragg's reflections of sphere structure of metallic gold respectively (JCPDS no. 04-0784) [29]. The broadening of Bragg's peaks indicates the formation of AuNPs. Nearly monodispersed AuNPs with controllable size and uniform shape can be easily obtained in the simple aqueous reduction method.

3.2. The AuNPs Photocatalytic study for reduction of Methylene Blue

Contamination of water with organic dyes has

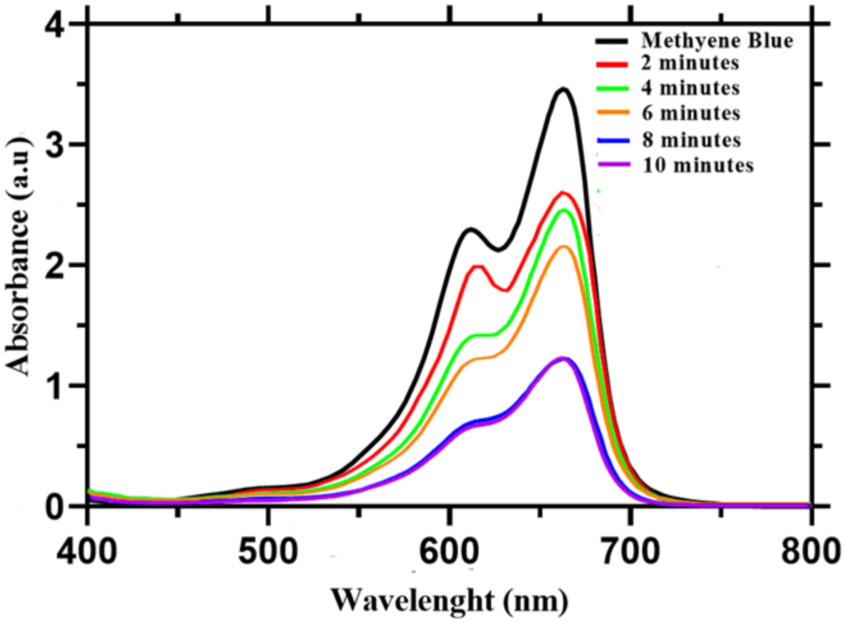

Figure 5. Absorbance spectra of photocatalytic degradation for MB dye in the presence of AuNPs

Table 1. The DPPH scavenging activity of synthesized AuNPs

Sample	Concentration (μg/ml)	DPPH scavenging activity (%)
P. dioica leave aqueous extract	50	68.87 ± 0.21
	100	72.37 ± 0.15
	150	78.15 ± 0.31
AuNPs	50	10.61 ± 0.10
	100	18.54 ± 0.24
	150	37.43 ± 0.42

become a formidable challenge in recent years. Methylene blue (MB) was chosen as the subject of our study because it is one of the most widely used organic dyes in many industries, and its residue in wastewater is considered toxic contamination. The MB was widely used in industry as a redox indicator, and the traditional method for removing it from wastewater was to use a reducing agent like $NaBH_4$, which produces hydrogen gas through a hydrolysis reaction in aqueous solution. The catalytic activity of AuNPs in the presence of $NaBH_4$ is investigated in this study. The absorption spectrum of MB is well known for having a peak at 664 nm attributed to the n-π* transition and another shoulder peak at 614 nm [29]. In the presence of $NaBH_4$, this peak gradually decreases due to the formation of the reduced form known as leuco methylene blue (LMB) [37]. Nonetheless, it was discovered that the rate of reduction by $NaBH_4$ was slow and prolonged. AuNPs have been used as a catalytic material. The resulting absorption spectra is plotted in Figure 5. The blue color of the MB and $NaBH_4$ solution was observed to vanish when sample from prepared AuNPs was added to the solution. After two minutes, the intensity of the peak at 664 nm reduced, indicating that the AuNPs were an active catalyst for MB reduction. Following the control sample ($NaBH_4$ solution without any AuNPs), a 73% reduction was obtained after eight minutes and it remained unchanged for ten minutes. Accordingly, a clear improvement and enhancement were obtained due to the addition of the AuNPs.

3.3. Antioxidant activity

It has been documented that a reactive oxygen species and other free radicals may be formed and released during a variety of biological processes, resulting in pathogenicity [36][37]. Antioxidant behavior refers to the formation of non-reactive and stable radicals as a result of the inhibition of any molecule's oxidation mechanism. This is accomplished by preventing the oxidative chain reaction's initiation step. As a result, considerable effort was expended in the quest for an antioxidant agent capable of obstructing or preventing oxidative harm [40]. It was recently discovered that AuNPs, especially those prepared in a green route, have significant antioxidant potential, which is dependent on the properties of various phytochemicals encrusted on the surface of the AuNPs [24][39][40]. The DPPH assay is a quick and easy way to figure out the preliminary results. The synthesized AuNPs in this study have a higher propensity for scavenging DPPH (Table 1). The colloids scavenging action increases as the concentration of the synthesized gold colloid rises. Tannins and polyphenols are abundant in the aqueous extract of *Pimenta dioica* leaves [27]. These bioactive compounds synergic activity as a reducing and stabilizing agent has been predicted.

3.4. Antibacterial activity

Noble metals and their compounds have antimicrobial properties, allowing them to be used to treat burns and chronic wounds. Metal nanoparticles' superior biological performance can be due to their high surface area to volume ratio as compared to their bulkier counterparts [43]–[45]. The antibacterial activity of synthesized AuNPs was tested on a variety of bacteria in this study under agar well diffusion method. Table 2 shows antibacterial effect of bioinspired AuNPs on different human pathogens *S. aureus* and *E.coli*. For an addition of 30 μg/ml of the gold colloid, an

Table 2. Antibacterial activity of AuNPs

Bacteria	Zone of Inhibition (mm)				
	Distilled water	Amphotericin B (20 µg/ml)	AuNPs (10 µg/ml)	AuNPs (20 µg/ml)	AuNPs (30 µg/ml)
Staphylococcus aureus	-	12 ± 1.0	-	2 ± 1.0	4 ± 0.5
Escherichia coli	-	14 ± 1.0	2 ± 0.5	6 ± 1.0	9 ± 1.0

inhibition zone of 4 mm *S. aureus* and 9 mm for *E.coli*. The mechanism behind AuNPs' bactericidal effect has yet to be fully investigated. However, earlier studies cite many reasons for the impact in a hazy depiction of the process. AuNPs have been documented to bind to the cell membrane's surface and disrupt key functions such as permeability and respiration, resulting in antioxidant depletion and the development of reactive oxygen species (ROS) [46]. Metal nanoparticles can also release metal ions, which can penetrate the cell wall and cause DNA damage and protein malfunction. The surface area available for touch determines how well the particles stick to the bacteria. As a result, smaller AuNPs with a higher surface area will have a stronger bactericidal impact than larger AuNPs [47]. The present study clearly indicates that the synthesized AuNPs show good activity against both gram-positive and gram-negative bacteria.

4. CONCLUSION

In summary, AuNPs were successfully biosynthesized by an inexpensive, fast, and safe approach, using *Pimenta dioica* leaves aqueous extract, without the use of any toxic chemicals. TEM imaging revealed that these AuNPs have spherical structure. Moreover, FTIR analysis suggested that the surface of AuNPs is covered by biomolecules found in the plant extract such as phenolics and eugenols. These AuNPs have demonstrated an excellent catalytic activity for the degradation of MB. Additionally, AuNPs displayed the most potent antioxidant potential. Also, an antibacterial inhibition was evident against gram-positive and gram-negative pathogenic.

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